Conversion of Carbon Dioxide into Fuel by Electrochemical Reduction In Aqueous Solvents

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Abstract

The mission of Omnidea, a Portuguese SME is to perform leading edge R&D in innovative energy concepts. In collaboration with Research Institutes Omnidea is developing a technology based upon a regenerative energy storage cycle. In this cycle the recharge system converts CO_2 into hydrocarbons using a renewable source of power. The discharge system produces electrical energy when hydrocarbons and oxygen from the recharge system are directly supplied to a device such as a Solid Oxide Fuel Cell (SOFC). This work focuses on the challenges involved in the task of bringing this technology closer to the market. A key feature of this technology is the use of copper which is known to have unique properties for converting CO_2 electrochemically into hydrocarbons. The modification of copper electrodes with copper deposits to improve the catalytic activity and selectivity of the cathodes in the production of hydrocarbons in aqueous solvents is also described.

Keywords: *CO_2, copper, electrodeposition, electrochemical reduction, catalysts, energy*

1 Introduction

The energy cycle envisaged in this work consists in a recharge system, which is composed of an electrochemical cell that converts CO_2 into hydrocarbons using a renewable source of power such as solar power. The discharge system produces electrical energy when hydrocarbons and oxygen from the recharge system are directly supplied to a device such as a Solid Oxide Fuel Cell (SOFC), or to an internal combustion engine.

Such type of energy cycles can contribute to the efforts that are continuously being made to reduce the emission of greenhouse gases, especially CO_2 by turning a problematic waste product into useful fuel. Moreover, such an approach is also useful for space applications, namely Mars exploration missions since the Martian athmosphere is composed of 95% CO_2. For a return mission to Mars an In Situ Propellant System (ISSP) using this cycle would allow to produce fuel from athmospheric CO_2 and oxygen from Martian ice. The discharge system would make available energy for life supporting systems and surface power.

Worldwide commitments to reduce CO_2 emissions to pre-1990 levels in the next 12 to 13 years pose a formidable challenge. To make this goal economically feasible, development of new technologies is essential.

The ideal process to convert CO_2 into fuel should have few process steps, be easily scalable, work at room temperature and be cost effective. Electrochemical reduction of CO_2 is a technology with potential to meet these goals.

Direct conversion of CO_2 to hydrocarbons was first reported in 1985 by Hori *et al*. using 99.99% pure copper as a cathode with 0.5 M $KHCO_3$ electrolyte for the electrochemical reduction of CO_2 at ambient temperature and current density of 5.0 $mAcm^{-2}$ for 30 to 60 minutes with Faradaic efficiencies for CH_4 of 37 to 40**%** [1].

The reduction of CO_2 to hydrocarbon products is a complex multi-step reaction. Its mechanism has not been completely elucidated yet [2]. The faradaic efficiencies of the process are strongly dependent of the surface structure and local conditions, such as pH, $KHCO_3$, and CO_2 concentration and electrolysis time [3].

Although research in CO_2 electrochemical reduction has been undertaken for more than twenty five years, the electrochemical reduction of CO_2 at copper electrodes has not yet been developed and implemented at a scale for demonstration and actual system applications. This is mainly due to the low current densities and or low Faradaic efficiencies exhibited by the state of the art systems.

This work focuses on the challenges involved in the task of bringing this technology closer to the market and the lines of research followed to meet these challenges.

2 Experimental

Reduction of CO_2 was performed potentiostatically in a flat cell at room temperature and atmospheric pressure. Electrolysis was carried out with continuous CO_2 flow (14.78 cm^3 min^{-1}). The electrolyte solution was 0.1 M $KHCO_3$ (Merck pa.). A cation exchange membrane separated the cathode and anode compartments. The anode was a Pt mesh (from Goodfellow metals). A copper mesh (Goodfellow Metals) and copper modified electrodes (Omnidea Lda) were used as working electrodes. The nominal electrodes dimensions were ca. 2 cm^2.

The electrode potencial was measured with a Ag/AgCl reference electrode.

The gasous products of the electrochemical reduction were analysed by online gas chromatography. A 4890D GC from Agilent equipped with a thermal conductivity detector TCD and a 6-port gas sampling valve with a 0.250 mL loop was used.

The faradaic efficiencies were calculated on the basis of the numbers of electrons required for the formation of one mole of product from CO_2 and H_2O; 2 electrons for CO, 2 electrons for H_2, 8 electrons for CH_4, 12 electrons for C_2H_4 and 14 electrons for C_2H_6.

3 Results and Discussion

A key feature of the technology under development is the use of copper which is known to have unique properties for converting CO_2 electrochemically into hydrocarbons. The modification of copper electrodes with copper deposits to improve the catalytic activity and selectivity of the cathodes in the production of hydrocarbons in aqueous solvents was one strategy followed. This strategy proved to be successful [4].

Fig. 1 shows the gaseous products obtained from the electrochemical reduction of CO_2. By controlling the characteristics of the electrodeposits, mainly the surface area, ethylene (C_2H_4) and ethane (C_2H_6) can be selectively produced without any methane (CH_4) (case 3 in Fig2) yielding fuels with a higher volumetric energy density (6.67 kWh/l for ethane as opposed to 3.38 kWh/l for methane), Fig2. Furthermore, it was shown that the presence of the electrodeposits leads to a steady stable flow during 4 hours of hydrocarbons from the reduction of CO_2.

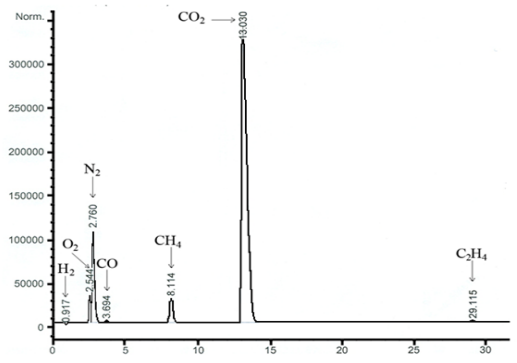

Fig. 1. Products of electrochemical reduction of CO_2. Analysis of components by gas chromatography.

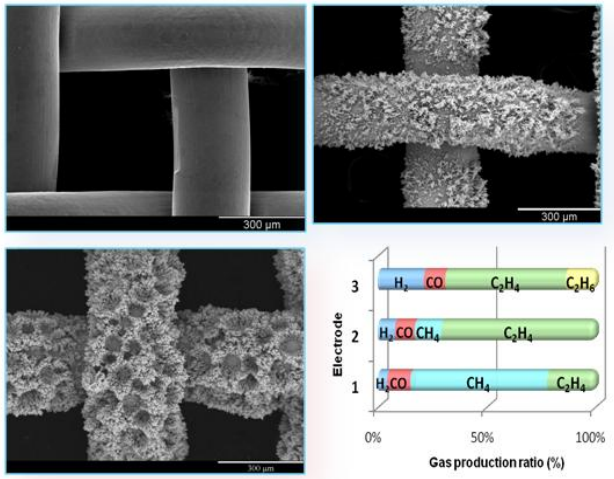

Fig. 2. Volumetric ratio of products for different electrode modifications, 1-3.

Nevertheless such performance must still be significantly improved to be used in commercial applications. Electrodes should not be easily deactivated - this is one obvious system requirement. In fact this is one of the most serious problems in a practical use of this process. It has been pointed out that the Faradaic efficiencies for hydrocarbons rapidly decrease about 30 minutes after the start of the electrolysis and the electrode becomes almost completely inactive at longer times [5]. Electrode deactivation was attributed to the deposition of poisoning species such as graphitic carbon [6-7], adsorbed organic intermediates [5], or copper oxide [8].

4 Conclusions and Future Prospects

Omnidea is targeting an electrochemical reduction system in which CO_2 reduction would not need a significantly more negative voltage than the thermodynamic requirements to improve the energy conversion efficiency of this technology. To achieve this goal, electrocatalysts exhibiting simul-

taneously reversible reduction characteristics, high faradaic efficiencies or selectivity and high reaction rates are needed. Further developmental work is being carried out under the FP7-NMP program entitled CO_2 Loop for Energy Storage and Conversion to Organic Chemistry Processes Through Advanced Catalytic Systems (CEOPS).

5. References

[1] Hori, Y., Kikuchi, K., Susuki, S. Production of CO and CH_4 in Electrochemical Reduction of CO_2 at Metal Electrodes in Aqueous Hydrogenocarbonate Solution, *Chem. Lett*. pp.1695-1698, 1985

[2] Gatrell, M., Gupta, N., Co A., Electrochemical Reduction of CO2 to Hydrocarbons to Store Renewable Electrical Energy and Upgrade Biogas, *Energy Conversion and Management* 48, pp1255-1265, 2007.

[3] Gatrell, M., Gupta, N., Co A., A review of the aqueous electrochemical reduction of CO_2 to Hydrocarbons at Copper, *Energy J. of Electroanalytical Chemistry,* 594, pp1-19, 2006.

[4] Gonçalves, M. R., Gomes A., Condeço J., R. Fernandes R., Pardal T., C.A.C. Sequeira C.A.C., Branco J.B. Selective electrochemical conversion of CO_2 to C_2 Hydrocarbons, *Energy Conversion and Management*, 51, pp 30-32, 2010

[5] Kyriacu, G. Anagnostopoulos, A., Electroreduction of CO_2 on Differently Prepared Copper Electrodes, *J: Electroanal. Chem.* 322, pp 233-246, 1992

[6]. Cook, R. L., MacDuff, R. C., Sammels, A. F Electrochemical Reduction of Carbon Dioxide to Methane at High Current Densities. *J: of Electrochem. Soc.*, 134, pp 1873-1874, 1987

[7]. DeWulf, D. W., Jin, T., Bard, A., Electrochemical and Surface Studies of Carbon Dioxide Reduction to Methane and Ethylene at Copper Electrodes in Aqueous Solutions, *J: of Electrochem. Soc.*, 136, pp 1686-1691

[8]. Shiratsuchi, R., Aikoh, Y., Nogami, G., Pulsed Electroreduction of CO_2 on Copper Electrodes, *J: of Electrochem. Soc.* 140, pp 3479-3482, 1993